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PHOTOCHEMICAL PROBLEMS OF THE VENUS ATMOSPHERE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

An experimental program to develop an understanding of the
chemical processes occurring in the Venus atmosphere is in progress.
Although the exact chemical composition of the Venus atmosphere is
not known, it is known that CO_2 is a major constituent, CO and O_2 are
minor components and there are probably substantial amounts of N_2 and
some noble gases. Water vapor seems to be almost entirely absent.
At present there is no evidence for other gaseous constituents. In
the Venus chemosphere CO_2 will be dissociated into CO and O-atoms and
at higher altitudes N_2 and CO will be dissociated into atoms. These
may recombine in several different ways. Experiments using both
ultraviolet light and ionizing radiation have been carried out to
supplement the information available in the literature on the mech-
anisms of these recombination reactions. Absorption coefficients of
CO_2, CO, and O_2 have been determined in the region from 1850 to 4000
A.

In connection with the recently publicized ''high tempera-
ture'' of Venus, it should be noted that there are a variety of
alternate, nonthermal mechanisms to which the observed microwave

radiation can be attributed. The possibility of chemical origin of the microwave emission is discussed and preliminary experiments indicate that such an explanation may be feasible.

It is of interest that the atmosphere of Venus is chemically inert, being neither oxidizing nor reducing. This situation can be understood if Venus initially had a reducing atmosphere, as proposed by Urey and others, with excess CO. Under these conditions, over geologic ages, the CO would have been converted by the solar radiation to carbon suboxide polymer and to CO_2. Thus, carbon suboxide polymer may cover the surface of Venus. Thermal decomposition of the suboxide may have occurred to a greater or lesser extent depending on the surface temperature. Such a polymer may be a major constituent of the visible clouds obscuring the surface from view. Even today carbon suboxide polymer may be forming and decomposing in an equilibrium steady state. Some other possible components of the cloud layer are suggested.

Since Venus apparently does not rotate, the dark side may be substantially cooler than the bright side; however, the difference may be less than anticipated from analogy with the Earth, because on the surface of a non-rotating planet, heat transfer by convection will be much more efficient than on a rotating planet. If the temperature on the dark side is very low ($\sim 234°K$) and the partial pressure of CO_2 is about 10 atmospheres, as some have proposed, CO_2 may condense into liquid oceans.

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INTRODUCTION

The planet Venus is the nearest of the planets to Earth and in many ways can be regarded as a ''twin'' of Earth. Despite these facts, less is known about Venus than almost any other planet in our solar system, with the exception of Pluto. The principle reason for this mystery is the cloud layer covering the planet, which completely obscures the surface from view. Our direct knowledge of the nature of the temperature, pressure, chemical composition, and other conditions existing on Venus is confined to the region above the cloud layer. All information about the nature of the conditions at the surface of the planet must be derived from our knowledge of conditions above the cloud layer; the state of this knowledge is such that widely divergent views are possible.

It is the purpose of the work described in this paper to develop an understanding of the chemical processes occurring in the Venus atmosphere in the light of available data on atmospheric constituents, nature and abundance of impinging solar radiation, and the nature and rates of various possible competing chemical reactions.

The first information about the constitution of the Venus atmosphere came in 1932 when Adams and Dunham detected strong absorption bands of carbon dioxide (for discussion see Dunham, 1952). Since that time a number of workers have searched unsuccessfully for other constituents. In the past year the presence of traces of oxygen has been reported by Prokofiev and Petrova (1962), and Sinton (1962) has observed a small amount of carbon monoxide. Traces of water vapor have been reported, but this result is uncertain because it is based on one observation from a balloon without precise correction for water vapor in the Earth's atmosphere (Strong, 1961). These data are summarized in Table I. It is striking that oxygen and carbon monoxide, the decomposition products of carbon dioxide, are present in such small amounts. It should be noted that nitrogen is expected to be present in relatively large amounts because of its high cosmic abundance, since

Table I

Abundance of Constituents of the Venus Atmosphere

Constituent	Abundance above Cloud Layer	Reference
CO_2	10^5 cm atm	Dunham (1952), Herzberg (1952)
O_2	(a) < 100 cm atm (b) detected	Dunham (1952) Prokofiev and Petrova (1962)
CO	(a) < 100 cm atm (b) a few cm atm	Kuiper (1952) Sinton (1962)
H_2O	~ 2.5 cm atm	Strong (1961)
N_2O	< 100 cm atm	Kuiper (1952)
NH_3	< 4 cm atm	Kuiper (1952)
CH_4	< 20 cm atm	Kuiper (1952)
C_2H_4	< 3 cm atm	Kuiper (1952)
C_2H_6	< 1 cm atm	Kuiper (1952)

it can neither escape from the gravitational field of Venus nor be consumed chemically. However, it is extremely difficult to detect by Earth-based measurements because of the strong absorption of the Earth's atmosphere in the far ultraviolet region where nitrogen absorbs. A future Mariner type probe may certainly carry suitable instrumentation for nitrogen detection and overcome this problem. Similar considerations apply to the rare gases, which should be expected to be present in abundances comparable to those in the Earth's atmosphere. However, the escape conditions for helium-3 and helium-4 would be more favorable on Venus than on Earth. Some efforts have been made to observe emission from N_2^+ in the night sky of Venus, but these have yielded somewhat uncertain results(Kozyrev, 1961; Newkirk, 1961).

To provide an additional basis for detailed discussion of the chemistry of Venus atmosphere, certain useful data can be obtained by laboratory experiments. The results of these experiments are described in the following section.

EXPERIMENTAL

1. Absorption Spectroscopy-Absorption Coefficients of CO_2, CO and O_2 between 1850 and 4000 A.

In considering the photochemistry of the Venus atmosphere the two things which must be first considered are the intensities of the various solar radiations impinging on the atmosphere and the absorption coefficients of the various atmospheric constituents for these radiations. The solar radiation intensities are well known for Earth (Johnson, 1961) and can be readily calculated for Venus by the inverse square law. Since the distance of Venus from the sun is about 0.7 that for the distance of the Earth from the sun, Venus receives about twice as much solar radiation as the Earth. Carbon dioxide, the major constituent*, is known to absorb fairly strongly below 1700 A

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*If it should be determined in the future that N_2 is more abundant than CO_2, the kinetics of the chemistry of the Venus atmosphere would remain virtually unchanged.

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with a maximum absorption coefficient of about 30 cm^{-1} at ~1450 A, corresponding to dissociation into CO and O (^1D). Absorption at wavelengths between 1700 and 2250 A, corresponding to dissociation into CO and O in their ground states has not been reported. However, this region is of paramount importance for the photochemistry of the Venus atmosphere, since even if the dissociation occurs with only a very small absorption coefficient (10^{-4} cm^{-1} or less), the increased solar radiation intensity at these wavelengths and the long path length through CO_2 would make it a very significant process. A knowledge of the magnitudes of the absorption coefficients of the minor constituents CO and O_2 in this wavelength region is similarly of great interest. To extend the information available in the literature, measurements also were made on these gases in the course of the present study. A Perkin-Elmer model 350 absorption spectrophotometer which covers the entire ultraviolet, visible, and near infrared regions with a short wavelength limit of about 1850 A was used. Absorption coefficients as low as 10^{-4} cm^{-1} can be determined with this instrument. We have measured absorption spectra of all the gases of interest for the Venus atmosphere in the region between 1850 and 4000 A. This supplements the data of Watanabe et al. (1953) whose results in general cover wavelengths below 1800 A. The gases measured included CO_2, CO, O_2, CH_4, H_2O, N_2O, NO, NO_2, SO_2, and NH_3[*]. Most of the gases were carefully prepurified to remove traces of impurities which might cause misleading results. This was particularly necessary in the case of carbon monoxide since even the research grade gas (obtained from Air Reduction Co.) contained several hundred ppm of iron carbonyl which absorbs strongly in the ultraviolet. The results obtained for CO_2, CO and O_2 are shown in Figures 1, 2, and 3.

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[*]Not all of these measurements are reported in this paper.
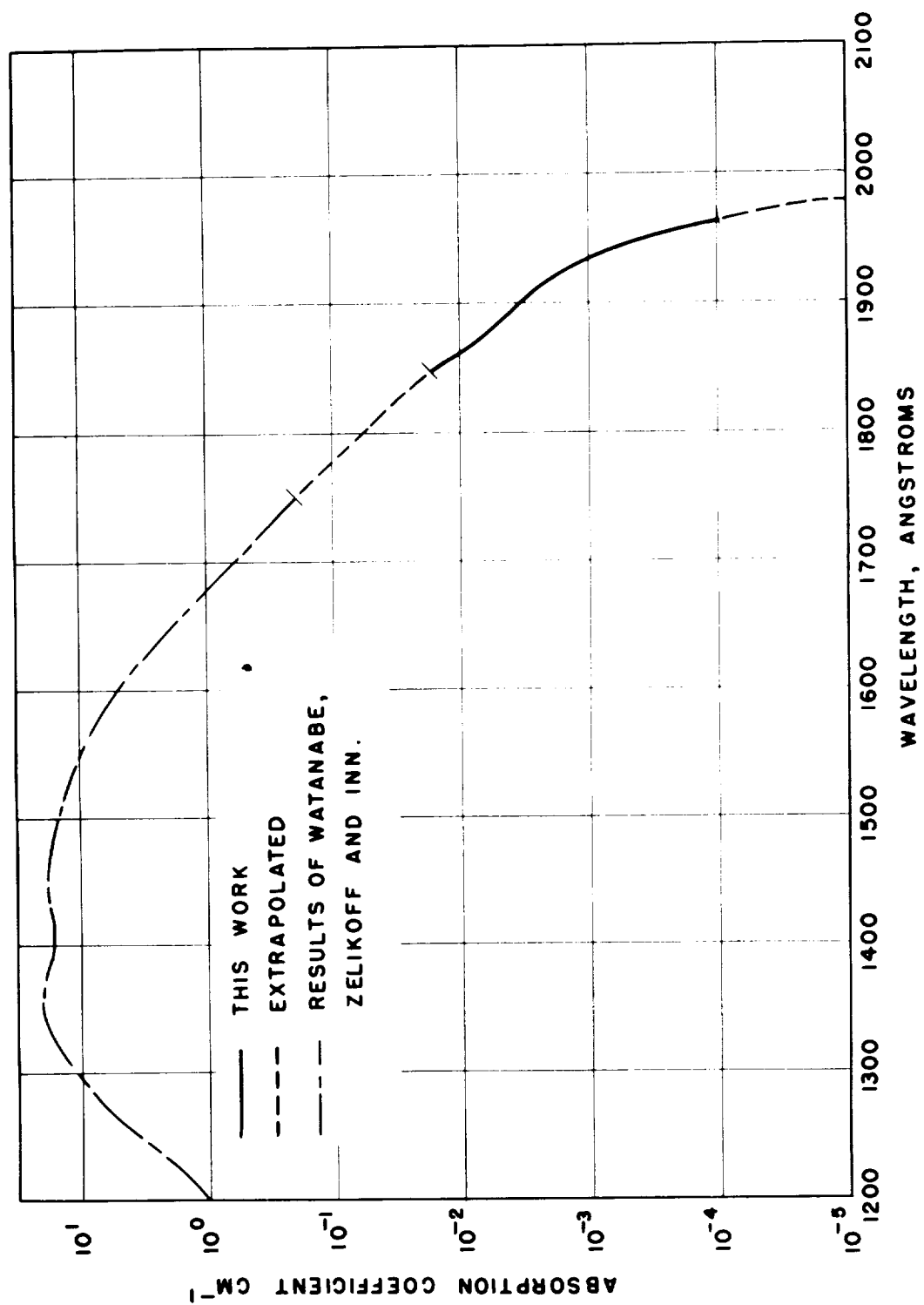
Figure 1 ABSORPTION COEFFICIENT OF CARBON DIOXIDE AS A FUNCTION OF WAVELENGTH

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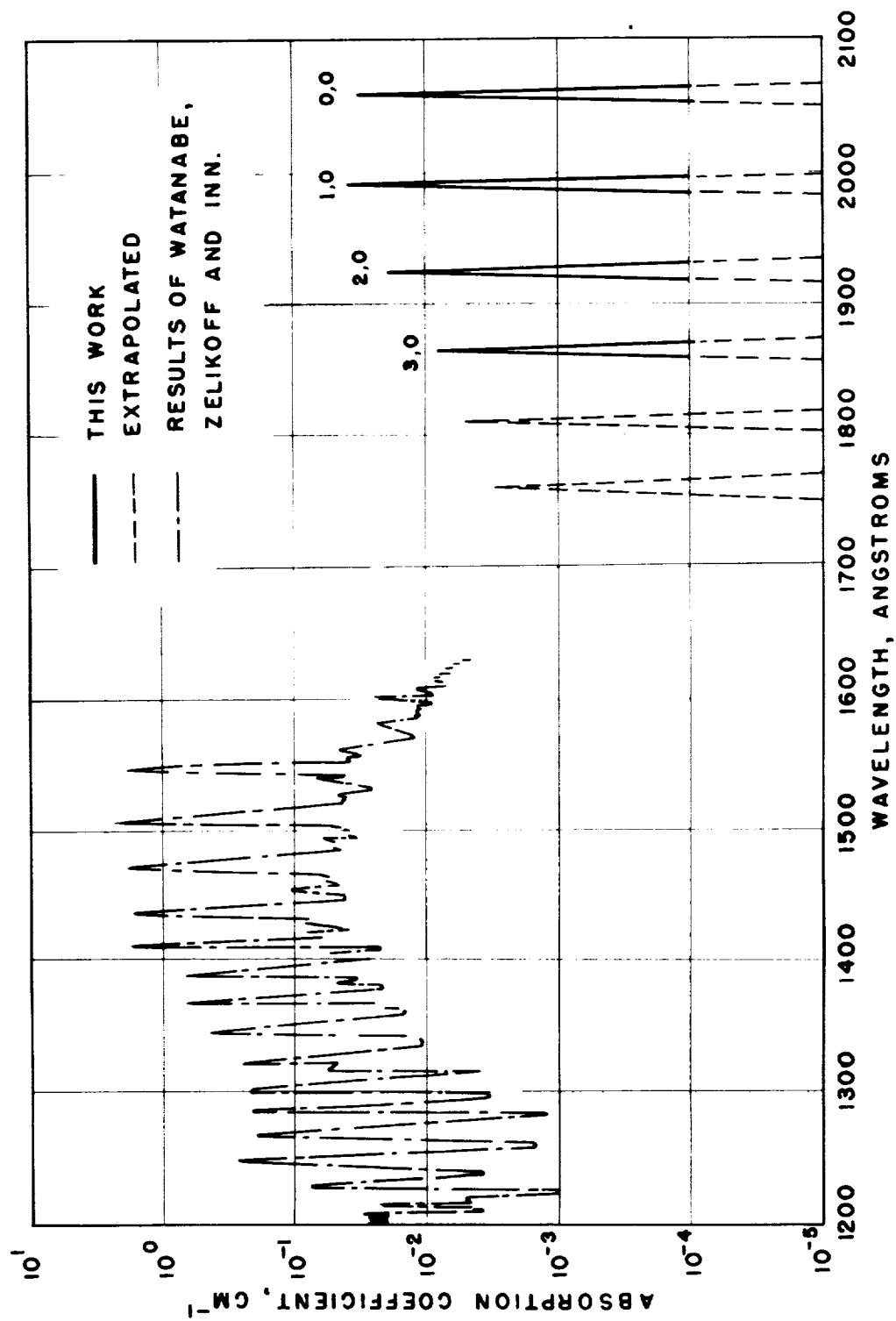
Figure 2   ABSORPTION COEFFICIENT OF CARBON MONOXIDE AS A FUNCTION
OF WAVELENGTH

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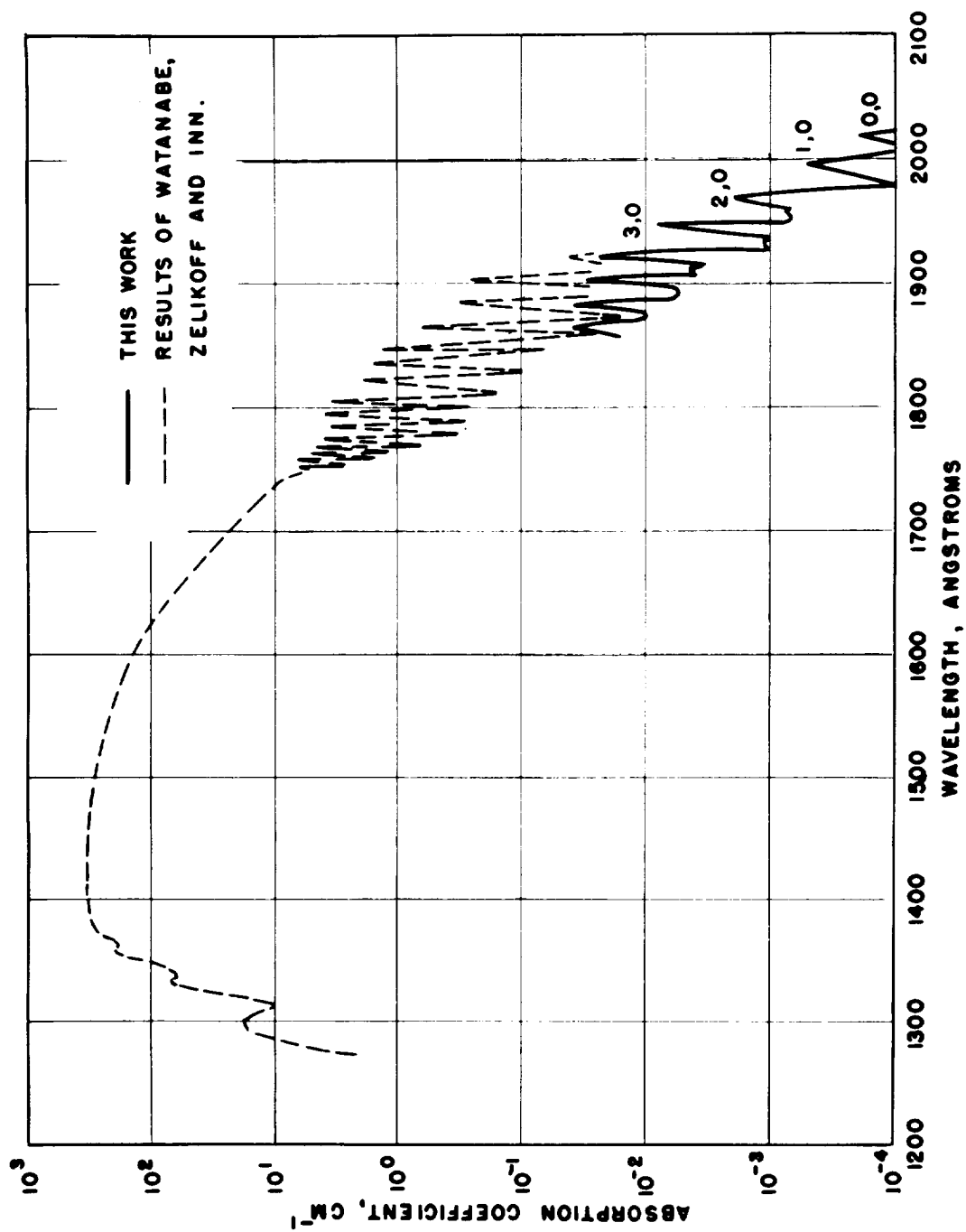
Figure 3 ABSORPTION COEFFICIENT OF OXYGEN AS A FUNCTION OF WAVELENGTH

CO_2 (Figure 1)

It was found that CO_2 begins to absorb at about 1960 A and gradually increases absorption with decreasing wavelengths. Between 1960 A and 4000 A no absorption could be detected, thus indicating an absorption coefficient of less than 10^{-4} cm^{-1} in this region.

CO (Figure 2)

Carbon monoxide is the gas with the highest binding energy known. Its dissociation energy of 11.11 eV corresponds to a wavelength of 1110 A. Thus no continuous absorption is to be expected in the entire range above 1110 A. The wavelengths which dissociate CO are energetic enough to ionize NO and are in the region normally referred to as ionizing radiation. In our work with CO we could observe the absorption peaks of the Cameron bands, representing the forbidden transition $X^1\Sigma \rightarrow a^3\Pi$, in the region between 1850 and 2060 A. It should be noted that the absorption coefficients for these bands are averages since the closely packed rotational structure within the bands is not resolved. Although these average absorption coefficients are rather low, it should be noted that if as much as 10 cm-atm of CO is present in the Venus atmosphere, about 3% of the impinging light quanta in the wavelength interval from 1850 to 2060 A could be absorbed. Since in this wavelength interval about 10^{13} light quanta per cm^2-sec are impinging on the atmosphere, as many as 3×10^{11} absorption processes may occur resulting in CO in the metastable $a^3\Pi$ state. The chemical reactions of this CO excited state are not known at present and constitute a rather interesting field of research.

O_2 (Figure 3)

In the case of oxygen, the data of Watanabe, et al. (1953) have been extended here to include the 0,0; 1, 0; 2, 0; and 3,0 Schumann-Runge bands in the region from 1920 to 2020A. In addition it was determined that the absorption coefficient in the wavelength

region above 2100 A must be less than 10^{-4} cm^{-1} since we were unable to detect any absorption.

2. Irradiation Studies

A. Ionizing Radiation

It is well known that carbon dioxide at atmospheric pressure is very resistant to decomposition by ionizing radiation (Harteck and Dondes, 1955; 1957; Lind, 1961), the radiation equilibrium with ionizing radiation being less than 0.1% decomposed[*]. The explanation proposed for this high stability involves regeneration via a carbon suboxide intermediate (see Table II). In the presence of an inhibitor, however, carbon dioxide becomes decomposed by ionizing radiation. An excellent inhibitor is NO_2; less effective inhibitors include SO_2 and I_2. It is not expected that NO_2 is present in the Venus atmosphere in view of the results obtained by Harteck (1957) and Dondes (1957) who studied the stationary concentrations of NO and NO_2 in a mixture of O_2 and N_2 subjected to ionizing radiation at various pressures. Extrapolation to low pressures shows that almost no NO or NO_2 is present. Harteck and Dondes (1958) have also investigated mixtures of CO_2 and N_2 at high pressures and find that since N-atoms do not react directly with CO_2, the stationary concentration of NO, NO_2 and N_2O is always less in a mixture of CO_2, N_2, and O_2 than in a mixture containing only N_2 and O_2. Therefore, NO and NO_2 should be absent from the entire atmosphere of Venus since the concentration must be less than that in the Earth's atmosphere where oxides of nitrogen play no role except as NO^+ in the ionospheric layers.

Carbon dioxide behaves in an entirely different manner with ultraviolet radiation such as the Xenon resonance line of 1470 A. As Groth (1937) working at atmospheric pressure, and Mahan (1960) and

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[*]Actually, under very clean conditions there is practically no stationary state of CO and O_2 as dissociation products, but since CO is polymerized to carbon suboxide in the gas phase a small amount of oxygen will remain from this process to inhibit further formation of suboxide.

Table II

Radiation Chemistry of Carbon Dioxide

(Harteck and Dondes, 1955)

$$CO_2 + h\nu \rightarrow \text{(a)} \quad CO + O \tag{1a}$$

$$\text{(b)} \quad C + O + O \tag{1b}$$

$$CO + h\nu \rightarrow C + O \tag{1c}$$

$$CO + C + M \rightarrow C_2O + M \tag{2}$$

$$C_2O + CO + M \rightarrow C_3O_2 + M \tag{3}$$

$$O_2 + O + M \rightarrow O_3 + M \tag{4}$$

$$C_3O_2 + O_3 \rightarrow CO_2 + O_2 + C_2O \tag{5a}$$

$$C_3O_2 + O \rightarrow CO_2 + C_2O \tag{5b}$$

$$CO + O + M \rightarrow CO_2 + M \tag{6}$$

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Jucker and Rideal (1957) at lower pressures, have shown, CO_2 becomes dissociated with a quantum yield of one. Since the solar radiation is a mixture of ionizing and ultraviolet radiation, it was necessary to make additional experiments. Initial experiments were carried out to investigate the effect of ionizing radiation at lower pressures on CO_2. It was convenient to do this with a glow discharge. As is well known, the effect of a glow discharge at low pressures is comparable to that of other modes of ionizing radiation.

The apparatus used consisted of a 22-liter Pyrex flask into which two aluminum electrodes were sealed, as shown in Figure 4. Both AC and DC discharges were employed, the power level in all cases being about 0.6 watts distributed over the vessel area. This power level was a compromise between the intensity of solar ionizing radiation and the need to reduce the time of experiments to a reasonable value. Under these experimental conditions the radiation intensity was about five times that of the ionizing radiation from the sun. The solar ionizing radiation intensity can be considered to be the total energy input for light quanta of wavelengths shorter than 1100-1200 A. This total ionizing radiation is equivalent to about 10^{12} ionization processes per cm^2-sec in the Venus atmosphere. Experiments were carried out at two initial CO_2 pressures, 500μ and 250μ. At the conclusion of each experiment the reaction mixture was passed through two traps cooled with liquid nitrogen, the second of which contained activated charcoal. Undecomposed CO_2 was frozen out in the first trap and dissociation products uncondensed at liquid nitrogen temperature were adsorbed on the charcoal. The final CO_2 pressure was determined and used as a measure of the extent of decomposition. The products adsorbed on the charcoal were analyzed mass spectrometrically and in all cases were found to be CO and O_2 in approximately the stoichiometric 2:1 ratio. At both pressures a rapid initial decomposition was observed which decreased as equilibrium was approached. At equilibrium the fraction decomposed was about 0.37 for 500μ initial pressure

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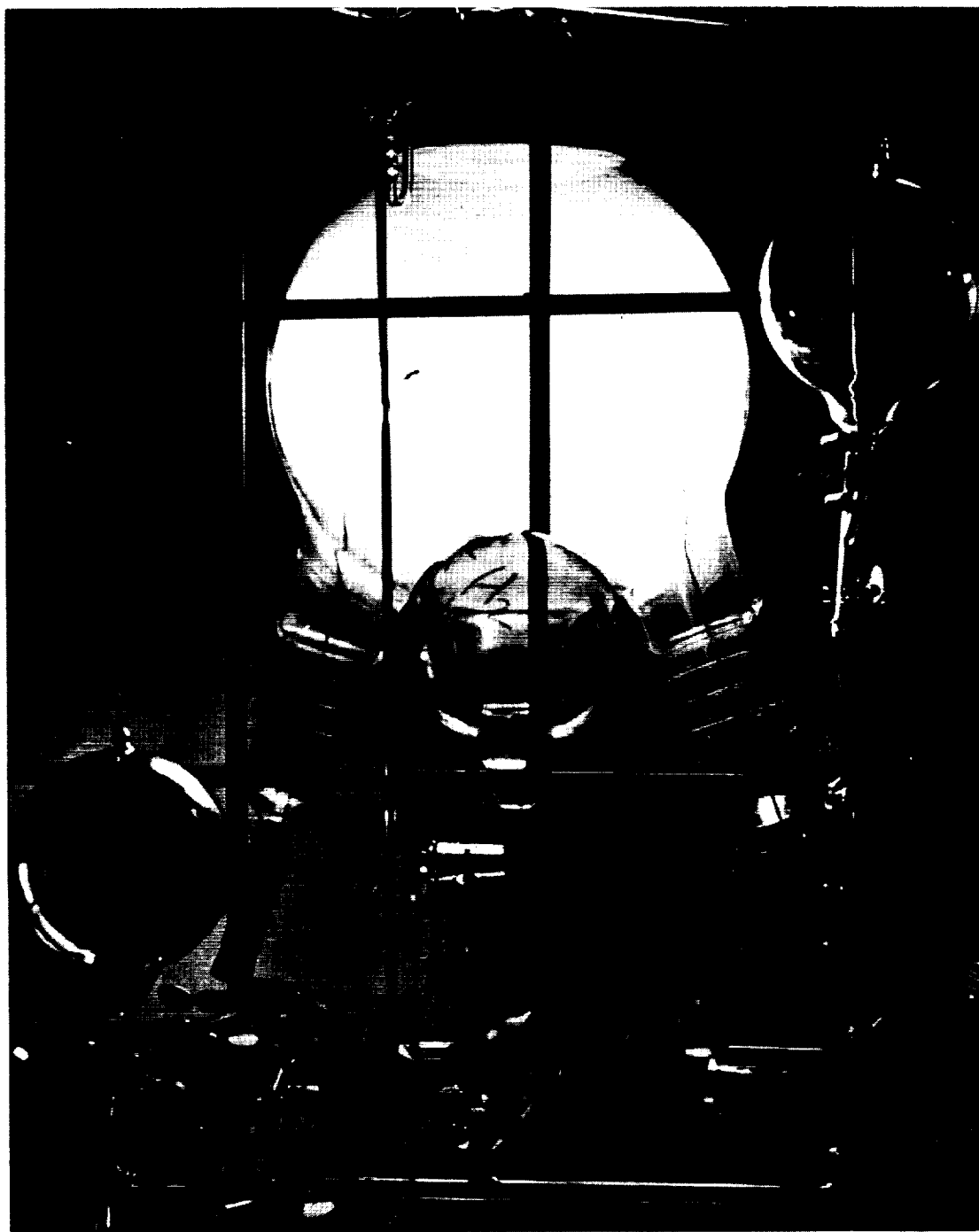
Figure 4 GLOW DISCHARGE THROUGH CARBON DIOXIDE IN 22-LITER
          FLASK

and about 0.50 for 250μ initial pressure. The presence of excess CO or O_2 initially did not change the position of the equilibrium significantly.

The chemosphere of Venus will exist, however, in a pressure range similar to that of the Earth, i.e., in a pressure range of a few microns. In connection with experiments described below, extrapolation can be made to the pressure range of microns or less showing that a quantitative dissociation of CO_2 and 0 should prevail.

To obtain experimental data over a larger pressure range and to determine whether the mode of ionizing radiation is important for the decomposition of CO_2, a series of samples was irradiated with mixed reactor irradiation (β,γ, and ionizing radiation caused by collisions with fast neutrons) in the Brookhaven reactor. The conditions were nearly identical to those used by Harteck and Dondes (1955, 1957) who irradiated CO_2 at higher pressures. The CO_2 pressure of these irradiated samples was varied from 250 mm down to 2.5 mm. The irradiations were carried out at room temperature which may not be too different from that of the Venus chemosphere. The time of the irradiations was sufficiently long that equilibrium should have been reached. After irradiation the CO_2 was frozen out and the pressure of the decomposition products was measured. These were then adsorbed onto charcoal and analyzed mass spectrometrically. The CO_2 pressure was then measured and was also mass analyzed, to check for impurities. Figure 5 shows a logarithmic plot of the ratio of CO_2 dissociated to CO_2 undissociated, as a function of pressure, including both the glow discharge and reactor irradiations. It is clear that dissociation increases rapidly with decreasing pressure and that the type of ionizing radiation is not important.

In addition a few experiments were made with mixtures of nitrogen and CO_2. As expected, there was no difference in the results because as discussed above, under these conditions the stationary concentration of NO_2, which may act as an inhibitor, is so low that no

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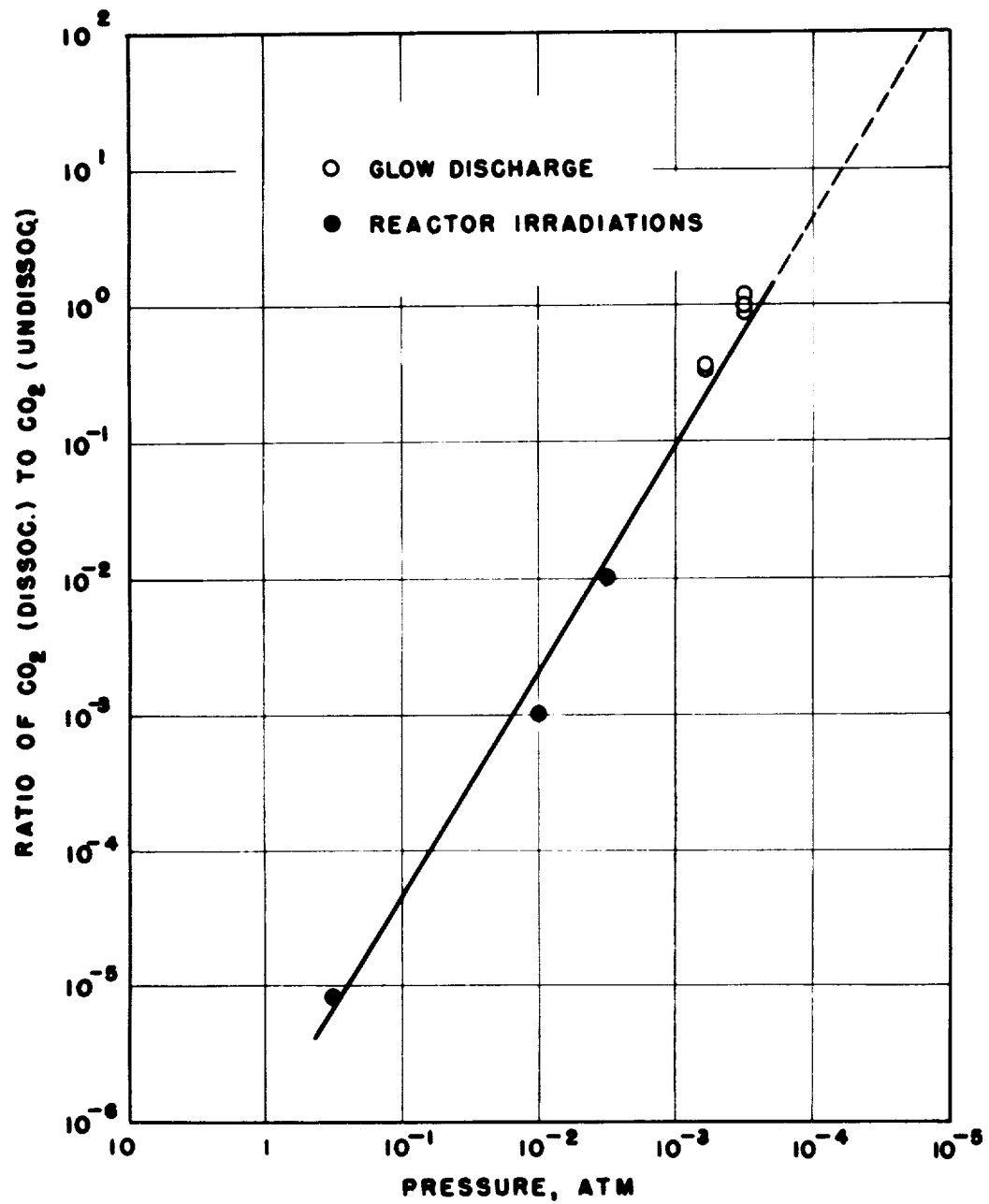
Figure 5 DISSOCIATION OF CARBON DIOXIDE BY IONIZING
RADIATION AS A FUNCTION OF PRESSURE

increased dissociation occurs. Therefore, even if substantial amounts of N_2 are present in the Venus atmosphere, these will not affect the photochemistry.

B. Mixed Ultraviolet Radiation

The ultraviolet spectrum can be divided into two regions for which the photochemical behavior of the Venus atmosphere will be enitrely different due to the nature of the absorption coefficients of CO_2 and O_2. In the region of wavelengths below about 1900 A, both CO_2 and O_2 will absorb with high absorption coefficients so that all of this ultraviolet radiation is absorbed at a pressure of a few microns. (See Figure 6). In this region, which has been very thoroughly investigated from the standpoint of the behavior of oxygen in the Earth's atmosphere, oxygen is almost entirely dissociated (N_2 does not absorb at all) and CO_2 will also be largely dissociated although its absorption coefficient is only about 0.1 that of O_2 (See Figures 1 and 3). Radiation in this region is thus responsible for the chemosphere which is a region of great interest.

At longer wavelengths the absorption coefficients of both CO_2 and O_2 are quite small and above 2250 A CO_2 cannot dissociate. Weak absorption by oxygen at these wavelengths can result in the formation of O_3, however, which absorbs strongly, regenerating oxygen atoms. This region is thus of great interest from the standpoint of determining whether the carbon monoxide formed in the chemosphere of Venus has a rather long lifetime in the lower levels of the Venus atmosphere or whether it is oxidized rapidly.

To answer this question, we have subjected pure CO_2 with a few percent argon added, and mixtures of 90% CO_2, 7% Ar, 2% O_2, and 1% CO to irradiation from a 500 watt, high pressure mercury lamp. The argon addition was made for mass spectrometer standardization purposes. The radiation from this lamp was analyzed with a Jarrell-Ash recording monochromator and it was found that the 2537 A line was almost completely self-reversed. The shortest line of high intensity was at 2253 A
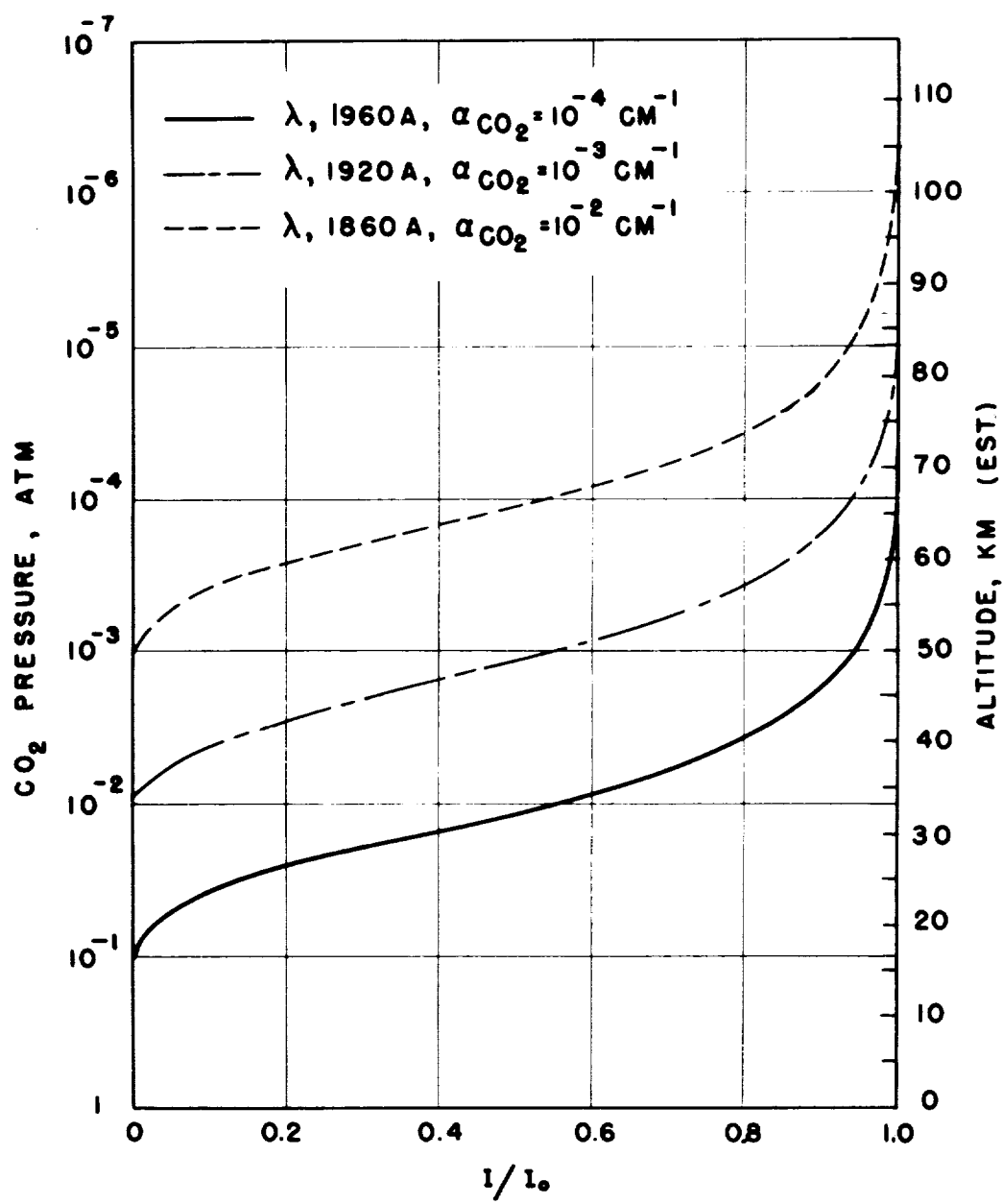
Figure 6 ABSORPTION OF SOLAR RADIATION IN THE
VENUS ATMOSPHERE

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wavelength since shorter wavelengths were absorbed by the cooling water jacket. The sample pressure in each case was about 500 mm. During each irradiation small samples were withdrawn at intervals, the CO_2 in each was frozen out with liquid nitrogen, and the uncondensed residue analyzed with the mass spectrometer. By recording the ratio of the peak heights at mass 40 to those at masses 32 and 28 any change in the CO and O_2 could be detected. It was found that both the CO and O_2 concentrations decreased with time and it was estimated that for each light quantum primarily absorbed by O_2, about one or two CO molecules become oxidized. With pure CO_2, no change was detected after irradiation for 24 hours confirming that no radiation was present sufficiently energetic to dissociate CO_2.

Under the same conditions mixtures of Ar, CO and O_2 but without CO_2, were irradiated and gave about the same rate of oxidation, about 1% per hour. Thus it appears that excited oxygen does not become deactivated by the presence of abundant CO_2, and the reverse reaction, which could have been postulated:

$$O_2(A^3\Sigma_u^+) + CO_2 \rightarrow O_2 + CO + O \qquad (10)$$
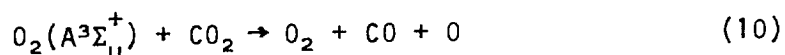
obviously does not occur.

When pure oxygen was irradiated, it was observed that a substantial equilibrium concentration of ozone was built up (4 mg/l.). When CO was present, practically no stationary ozone could be observed. This indicates that CO is oxidized to CO_2 via the oxygen-ozone cycle as shown in Table III.

KINETIC CONSIDERATIONS

On the basis of the experimental data certain conclusions can now be drawn about the state of the Venus atmosphere as a function of altitude, making comparisons with the Earth's atmosphere, under the assumption that no other chemical species, at present unknown, are present in the gas phase. The comparison is shown schematically in Figure 7.

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Table III

Oxidation of CO by the $O_2 - O_3$

Cycle in the Lower Atmosphere

$O_2 + h\nu \rightarrow O + O$	$h\nu \sim 2000 - 2400$ A	(7)
$O + O_2 + M \rightarrow O_3 + M$	$k = 5 \times 10^{-34}$	(4)
$O_3 + h\nu \rightarrow O_2 + O$	$h\nu \sim 2200 - 2800$ A	(8)
$CO + O + M \rightarrow CO_2 + M$	$k = 5 \times 10^{-36}$	(6)
$O_3 + O \rightarrow 2O_2$	$k = 10^{-14}$	(9)
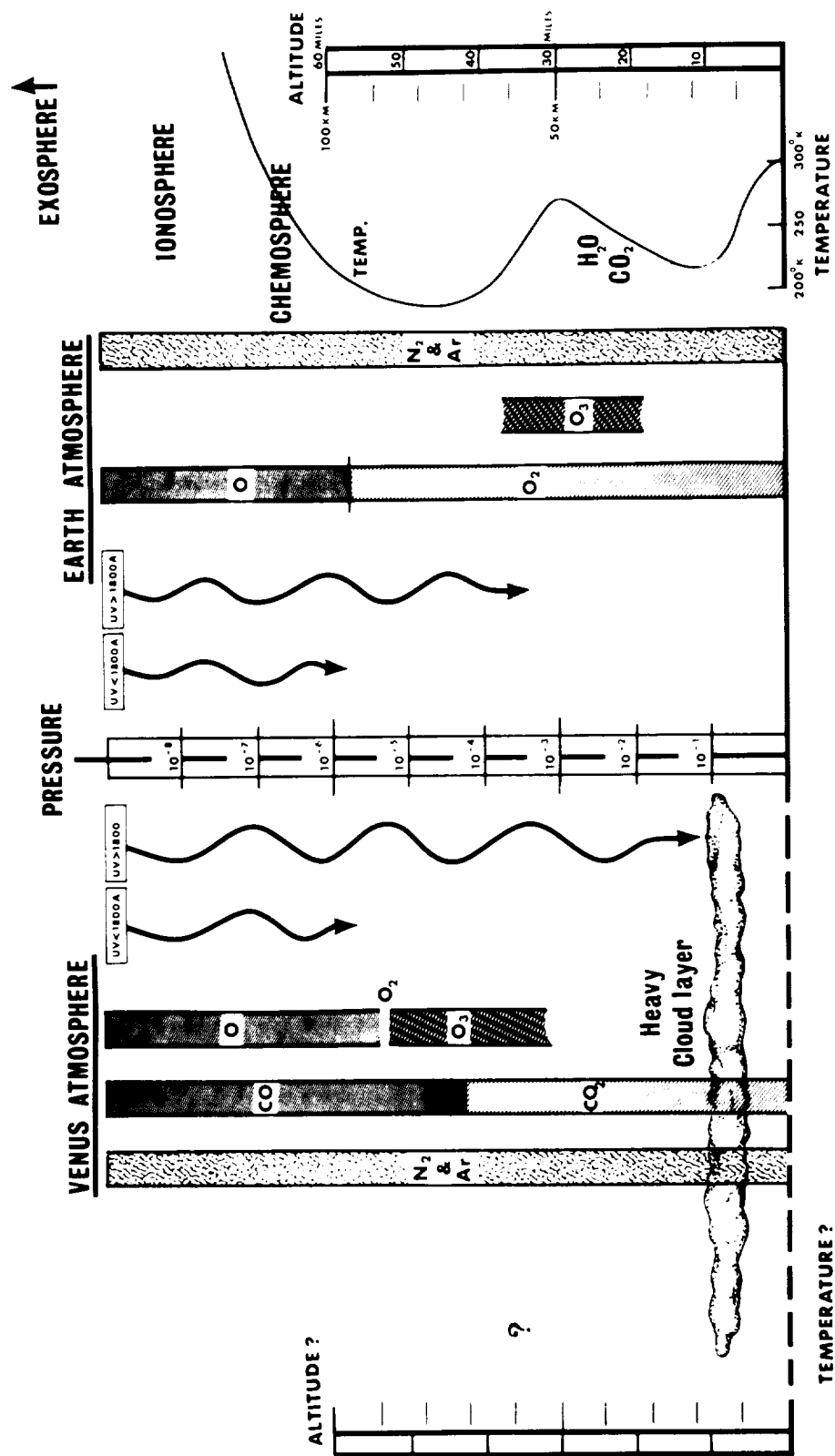
Figure 7   ATMOSPHERIC CHARACTERISTICS FOR EARTH AND VENUS

In the atmosphere there are three or four distinct levels. The highest is the exosphere from which molecules escape without collisions. Since Venus is very dry, no H-atoms formed by photo-dissociation of water vapor will be present in this region. However, a stationary H-atom concentration will exist due to the solar winds. This can be estimated as about 1/100 or 1/1000 of the H-atom concentration in the Earth's atmosphere. Since at 100 km (or 10^{-6} atm) in the Earth's atmosphere there are 3×10^7 H-atoms/cc, there may be about 10^5 H-atoms/cc at a corresponding altitude on Venus.

Below the exosphere is the ionosphere. Since the major constituent of the Venus atmosphere is CO_2, the Venus ionosphere will differ from that of Earth. High percentages of ions such as CO_2^+ and CO^+ may be expected. Other more complex ions may also be present.

The third region, the chemosphere, is the one in which the far ultraviolet radiation from about 1200 to 1900 A is strongly absorbed; above 1900 A the absorption coefficients for CO_2, O_2, and CO become small. In the Earth's atmosphere in this region solar ultra-violet radiation dissociates oxygen into oxygen atoms. Above 100 kilometers altitude most of the oxygen is in the atomic form. Recombination occurs mainly by three-body collisions such as

$$O + O + M \rightarrow O_2 + M \tag{11}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{4}$$

followed by

$$O_3 + O \rightarrow 2O_2 \tag{9}$$

At radiation equilibrium the total dissociation by light absorption must equal the total recombination:

$$\Sigma h\nu = \Sigma \text{ recombination} \tag{12}$$

The recombination rate is third order and therefore increases approximately as the third power of the pressure. On the basis of these facts

the altitude and pressure can be calculated at which the chemosphere begins. It may be emphasized that N_2 plays only a minor part in the chemosphere since its absorption coefficient is significant only in the region of 800 A wavelength and below.[*]

Similar conditions for a chemosphere will prevail on Venus. If CO_2 alone were present then dissociation would occur predominantly to CO and O-atoms and the following two competing recombination reactions would occur:

$$CO + O + M \rightarrow CO_2 + M \qquad (6)$$

$$O + O + M \rightarrow O_2 + M \qquad (11)$$

Reaction (6) is slow, however, by comparison to Reaction (11) by a factor of about 1000 at room temperature. This ratio will be somewhat temperature dependent because Reaction (6) has a heat of activation of several kcal. The situation in the Venus chemosphere is more complicated however, because molecular oxygen is formed by Reaction (11) and has a higher absorption coefficient than CO_2. Also, as seen in Figure 3, this absorption of O_2 extends somewhat further into the longer wavelength region.

The relative concentrations of CO_2, CO, O_2, and O-atoms in the Venus chemosphere and above can be estimated in the following way. In this region the rates of decomposition of CO_2 and O_2 which may be present are:

$$\frac{-d(CO_2)}{dt} = I \, \alpha'(CO_2) \qquad (13)$$

$$\frac{-d(O_2)}{dt} = I \, \alpha''(O_2) \qquad (14)$$

where I is the number of impinging light quanta capable of producing dissociation and α' and α'' are the absorption coefficients for CO_2

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[*]Kinetic data for the reactions of interest in the chemosphere have been presented in detail by Harteck and Reeves (1962).

and O_2 respectively. Similarly, the rates of formation of CO_2 and O_2 by three-body recombination[*] are given by:

$$+ \frac{d(CO_2)}{dt} = k' \ (CO)(O)(M) \tag{15}$$

$$+ \frac{d(O_2)}{dt} = k''(O)(O)(M) \tag{16}$$

where k' and k'' are the respective three-body rate constants. At equilibrium the rate of formation will be equal to the rate of decomposition for each component and therefore the following relationship will hold:

$$- \frac{d(CO_2)/dt}{- d(O_2)/dt} = \frac{+d(CO_2)/dt}{+d(O_2)/dt} \tag{17}$$

or

$$\frac{a'(CO_2)}{a''(O_2)} = \frac{k'(CO)}{k''(O)} \tag{18}$$

The ratio a'/a'' is about $1/20$ over the wavelength region of interest and the ratio k'/k'' is about $1/1000$, as noted above. Thus:

$$\frac{(CO_2)}{(CO)} \times \frac{(O)}{(O_2)} \approx \frac{1}{50} \tag{19}$$

From this is immediately apparent that in the region where the total pressure is about 10^{-7} atmospheres and the ratio $(O)/(O_2)$ is about 10, the ratio $(CO_2)/(CO)$ will be about $1/500$. It should be noted that the entire atmosphere above the chemosphere is equivalent to only about 1 cm-atm so that these considerations do not imply the presence of extensive amounts of atmospheric CO and O_2. As the pressure increases other recombination mechanisms will become significant and the above relationship will no longer be valid.

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[*]For simplicity we have assumed that three-body recombination predominates for CO_2 formation; however, it should be kept in mind that at low pressures two-body recombination may become important.

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The molecular oxygen formed in the chemosphere will be carried to lower regions of the atmosphere by diffusion and convection. Since it is known that oxygen is only a minor constituent of the Venus atmosphere, it cannot be continually built up by this photochemical process. Reoxidation of the carbon monoxide must therefore occur $\underline{via}$ the ozone cycle at these levels below the chemosphere as mentioned previously. As seen from Table III the O-atoms formed by Reaction (7) may simply cycle over the oxygen-ozone cycle:

$$O + O_2 + M \rightarrow O_3 + M \qquad (4)$$

$$O_3 + h\nu \rightarrow O_2 + O \qquad (8)$$

until reaction with CO occurs forming back CO_2 (Reaction (6)). The ozone molecule has a strong absorption in the ultraviolet region to almost 3000 A and will be dissociated within a few seconds while re-combination to ozone will depend on the total pressure and oxygen concentration and will vary from hours to fractions of a second. The extent to which reaction (9) occurs will depend upon the relative concentrations of O_3 and CO. The absolute concentrations of all constituents in the regions below the chemosphere will depend on diffusion and convection conditions which are at present unknown.

Carbon monoxide will become excited and dissociated by ultraviolet light in the upper atmosphere. It can be estimated that $10^{11} - 10^{+12}$ carbon atoms per cm²-sec are formed by ionizing radiation (assuming 10^{12} ionizing quanta/cm²-sec with a M/N value of ~ 1 for the decomposition of CO). These carbon atoms will obviously recombine with O-atoms forming CO in three-body collisions.[*] Similarly, reaction with CO to form carbon suboxide may occur:

$$CO + C + M \rightarrow C_2O + M \qquad (2)$$

Both reactions are third order and probably of similar rate.[**] As has

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[*]Reactions of carbon atoms with various gases have recently been studied by Dubrin, MacKay, and Wolfgang (1963).

[**]The reaction of carbon atoms with the small amounts of molecular oxygen present should be negligible, especially since the rate is slow (von Weyssenhoff, Dondes, and Harteck, 1962).

been shown by von Weyssenhoff, Dondes and Harteck (1962) the reaction
of carbon suboxide with O-atoms is exceedingly fast giving both

$$C_2O + O \rightarrow CO_2 + C \qquad\qquad (20a)$$

and

$$C_2O + O \rightarrow 2CO \qquad\qquad (20b)$$

Thus it appears that under existing conditions there is not much
possibility that carbon suboxide accumulates in the Venus chemosphere.
However, this statement deserves further critical consideration since
many data are not well enough known at present.

In addition, it has been shown (Lind, 1961; von Weyssenhoff,
Harteck, and Dondes, 1963) that excited CO molecules can react with CO
to give carbon suboxide or CO_2:

$$CO^* + CO \rightarrow \begin{array}{l} {}^{(a)}C_2O + O \qquad\qquad (21a) \\ {}^{(b)}CO_2 + C \qquad\qquad (21b) \end{array}$$
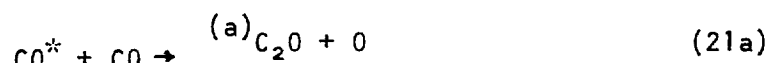
These reactions may also occur to a certain extent in the upper atmo-
sphere of Venus. Since the concentration of CO is low, there may not
be an opportunity for an excited CO molecule to react with a second
CO molecule, but alternate reactions may occur, such as with O_2 to form
$CO_2 + O$.

In the upper atmosphere of Venus nitrogen will be dissociated
into N-atoms and these may react with the carbon atoms produced by
dissociation of CO to form CN or cyanogen, C_2N_2. Under the action
of ionizing radiation cyanogen may polymerize to $(CN)_x$ or, in the
presence of oxygen, to $(CNO)_x$, a pale yellow solid (Lind, 1961). The
extent to which such reactions occur in the Venus atmosphere is not
now known and the possibility that such polymers may contribute to
the observed clouds should be considered.

MICROWAVE EMISSION

In the last few years radio astronomers have observed the
emission of radiation in the microwave region ($\lambda = 0.4 - 10.3$ cm) from

Venus (see, for example, Mayer, 1961 and Kuz'min and Salomonovich, 1962). This emission has been confirmed by the recent flight of Mariner II (Jet Propulsion Laboratory, 1963). The explanations which have been advanced to explain the origin of this radiation can be divided into two groups according to whether the origin is considered to be thermal (Sagan, 1960; Opik, 1961) or non-thermal (Jones, 1961; Tolbert and Straiton, 1962; Scarf, 1963). The most popular current explanation assumes that the microwave radiation is thermal in origin and corresponds to a high surface temperature for the planet. In particular, it is proposed that a high temperature ($\sim$ 700°K) does exist at the surface with very cold clouds ($\sim$ 230°K) above (Sagan, 1961; Jet Propulsion Laboratory, 1963; see also Kellogg and Sagan, 1961).

Prior to the discovery of the microwave emission, estimates of the temperature of Venus had been made based on a knowledge of the heat flux from the sun, the albedo of Venus, and estimates of the heat balance. The resulting temperature was found to be similar to that of Earth (Kuiper, 1952). A somewhat higher temperature might be estimated from our current knowledge that the planet rotates extremely slowly, if at all.

With the reports of emission of microwave radiation calculations of the temperature required for Venus to emit this radiation as a blackbody radiator have been made and it is from these calculations that the reports of 600°-700°K are derived. No other evidence for such high temperatures is known and all current models which postulate an insulating atmospheric blanket to justify such high surface temperatures seem more sophisticated than realistic. The absence of water vapor and the presence of very cold clouds constitute major stumbling-blocks to the acceptance of any ''greenhouse'' theory involving surface temperatures of the order of 700°K (Sagan, 1961; Kellogg and Sagan, 1961). It may be noted that Chamberlain and Kuiper (1956) have calculated a temperature of 285°K from the rotational structure of the 7820 A and

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8689 A bands in the CO_2 absorption spectrum of the Venus atmosphere. Spinrad (1962) has recently made a new calculation using the 7820 A band structure as recorded on plates obtained by Adams and Dunham (1932) and making slightly different assumptions. Spinrad's calculated temperatures range from 214°K to 445°K with the extreme values observed for the same phase angle. As Chamberlain and Kuiper (1956) have pointed out, the accuracy of an individual measurement of this type is rather low. Thus, the overall spread most likely results from errors inherent in the measurement rather than from true variations in the CO_2 temperature existing in the Venus atmosphere. Therefore, the average of all the values, 337°K, should be much less subject to error than the extremes, e.g., the 445°K emphasized by Spinrad.

Because of these fundamental difficulties involved in a thermal origin of the microwave emission and because the surface temperature is obviously of great importance for chemical and biological considerations, various non-thermal origins of the observed microwave radiation have been proposed (Jones, 1961; Tolbert and Straiton,1962; Scarf, 1963). However, these non-thermal models again have various drawbacks. Thus, it is appropriate to seek alternate sources for the microwave emission, and, as chemists, we have investigated the possibility of a chemical origin.

It is well known that the reaction of carbon monoxide with oxygen may result in emission of light both in form of bands and a strong continuum (See Gaydon, 1957). This reaction certainly occurs to a significant extent on Venus. The continuum is believed to arise from the reaction

$$CO + O \rightarrow CO_2 + h\nu \qquad\qquad (22)$$

Clearly, if only the spectrum of this radiation were considered in deriving a temperature for the reaction, an unreasonably high temperature would be obtained. Thus, an unexpectedly high emission in a certain spectral region should not be considered as black-body radiation

from the actual thermal temperature could be derived[*]. It must be kept in mind that a system in which chemical reactions occur is a system which is not in thermodynamic equilibrium.

Gaydon (1957 ; 1961) has proposed that the continuum emitted in the carbon monoxide-oxygen reaction occurs as the CO and O approach each other on a repulsive potential curve and drop down to the stable ground state. The continuum has been observed to extend to wavelengths as long as 9000 A (Feast, 1950) and there seems every reason to expect it to extend to much longer wavelengths. The question thus arises as to whether this emission extends into the microwave region, thus providing a possible chemical origin for the observed microwave emission from Venus. In addition, the possibility of other chemical reactions of a similar nature which may result in microwave emission should be considered. We now have in progress a survey program to evaluate the possibility of chemical reactions as a source of microwave emission.

Through the courtesy of the Naco Electronics Corporation we have been able to analyze the radiation from the various reactions for emission in the microwave region. As a matter of convenience we chose to examine the wavelength region between 2.8 and 4.1 cm (7.4 - 12 kMc/s known as X-band. The apparatus is shown in Figure 8. The system used had a lower detection limit of about 10^{-11} watts with about a 10 micron window. To date it has not been possible to observe any signal from reactions between atoms and molecules. However, from the discharge itself, signals were detected throughout the entire X-band using CO_2 or SO_2, although most gases such as air gave no signal. The intensity of this microwave emission corresponds to an unrealistically high blackbody temperature, in excess of $100,000°K$. It therefore seems probable that the Venus microwave emission may be caused, at least in

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[*]The ''high'' microwave emission observed at 10 cm wavelength would represent only 10^{-16} of the maximum intensity expected from a black-body radiator at a temperature of $600°K$ ($\lambda_{max} = 4.9$ μ)
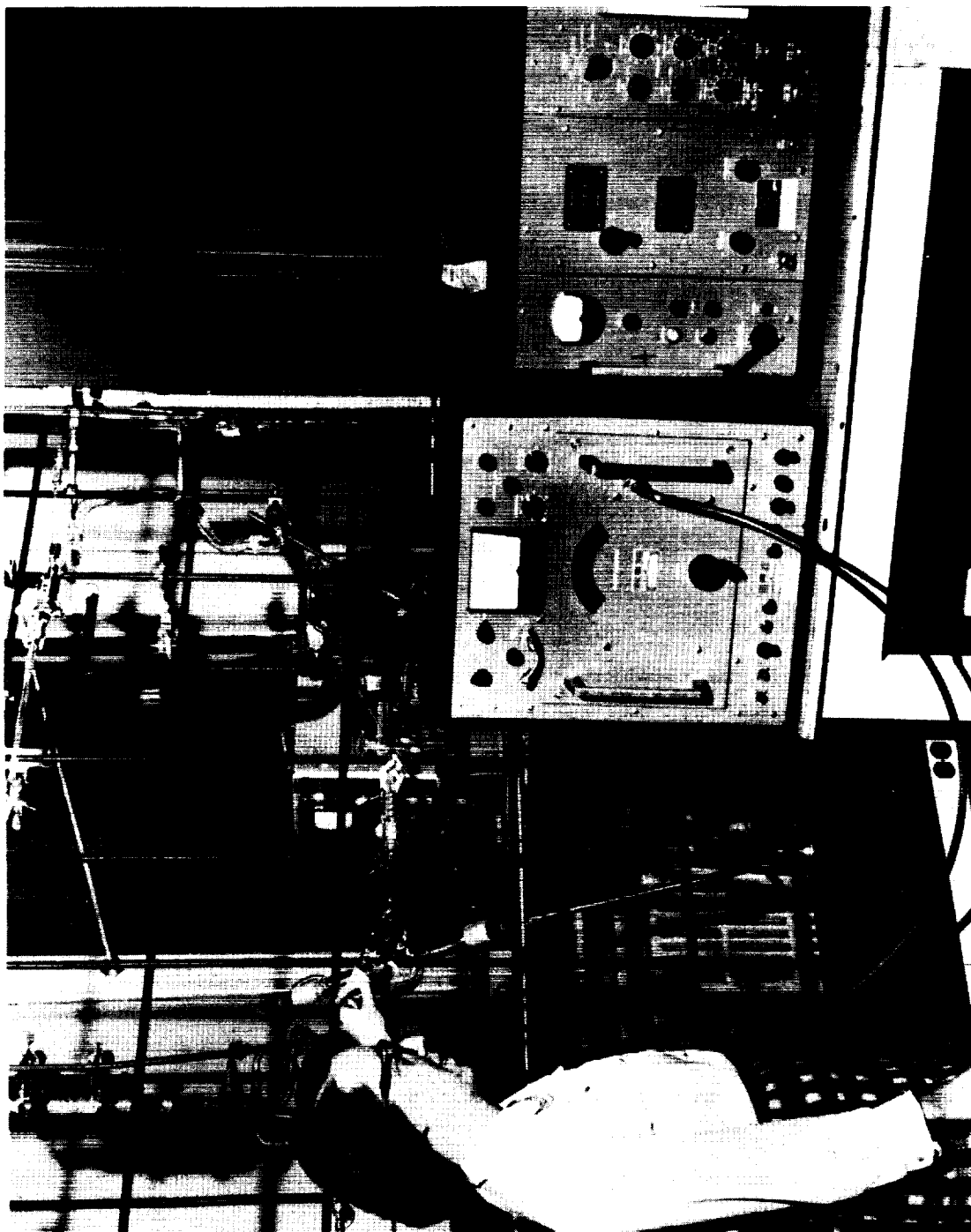
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Figure 8 EXPERIMENTAL ARRANGEMENT FOR STUDYING MICROWAVE EMISSION

part, by such a chemical source. Additional experiments utilizing more sensitive equipment are now in progress, especially searching for microwave emission from reactions occurring outside the discharge tube.

WATER AS A MINOR CONSTITUENT

The high atmospheric abundance of CO_2 in Venus is believed to indicate an absence of water on the surface of the planet since CO_2 is considered to be removed from the Earth's atmosphere, according to Urey (1952) by the equilibrium

$$MgSiO_3 + CO_2 \text{ (g)} \rightleftarrows Mg\ CO_2 + SiO_2 \qquad (23)$$
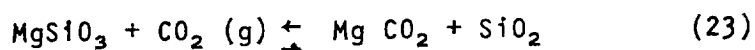
or similar reaction with calcium silicate. In the presence of liquid water the equilibrium is shifted strongly to the right, the equilibrium CO_2 pressure being about 10^{-4} atmospheres. In the absence of liquid water the reaction of CO_2 with silicates occurs either very slowly or not at all, thus leading to the conclusion that there is no significant amount of surface water on Venus. This assumes that the composition of the crust of Venus is about the same as that of Earth, which seems rather likely in view of the similar densities of the two planets.

In addition, the presence of large amounts of surface water would lead to significant amounts of atmospheric water vapor which would become photodissociated in the upper atmosphere and cause a build-up of atmospheric oxygen (Poole, 1941; Harteck and Jensen, 1948). Since this is not observed, any model incorporating either surface water or extensive atmospheric water vapor seems highly improbable.

It has long been known that the period of rotation of Venus is considerably longer than that of Earth and many astronomers have postulated that the period of rotation may even be equal to the period of revolution (224.7 days). The recent data obtained by Mariner II (Jet Propulsion Laboratory, 1962) on the absence of a strong magnetic field tend to support this conclusion. If it is assumed that one side

of Venus is forever turned toward the sun, then the dark side would be very cold. Thermocouple measurements of the infrared emission from the dark side of Venus give a temperature of $234^\circ K$ (Sinton and Strong, 1960). At this temperature liquid CO_2 has a vapor pressure of about 10 atmospheres, which is just the order of magnitude assumed in many models for the Venus atmosphere. Thus, under such conditions liquid CO_2 may be present as lakes or even oceans.

Such a large cold area would serve as a very efficient trap for water (vapor pressure at $234^\circ K$ is 0.0966 mm or about 10 parts per million of the CO_2) which could be present as an ice and snow layer on the lakes or as icebergs in the CO_2 ocean as well as an icy coating on the solid planetary surface. Small changes in temperature will result in strong evaporation and condensation of CO_2; such a situation would produce huge storms at the ''twilight'' zone. It must be emphasized that liquid CO_2 could be present only under the conditions of low surface temperatures on the dark side, high surface CO_2 pressure, and lack of planetary rotation. The temperature difference between the bright and dark sides may be substantially less than anticipated since on the surface of a non-rotating planet heat transfer by convection will be very efficient. In addition, it should be noted that if the planet rotates at all, even very slowly, little or no water in any form can be present, as previously discussed.

THE CLOUD LAYER

The composition of the clouds is a question which has been discussed for many years and still remains unsettled. Carbon suboxide has been suggested as a possible major constituent (Harteck and Groth, 1957) especially in the light of the suboxide mechanism proposed for regeneration of CO_2 in the presence of ionizing radiation. In the Venus atmosphere under present conditions, however, very little suboxide may be forming as discussed above. Nevertheless, it cannot be entirely excluded and further investigations should be made. However,

If Venus initially possessed a reducing atmosphere as proposed by Urey (1952) and Kuiper (1952), there may have been a time when the CO: CO_2 ratio was substantially higher than at present. Under these conditions, carbon suboxide polymer should have been formed in large amounts by the action of solar radiation on the CO. Thus not only clouds, but hills and dunes of suboxide polymer may exist on Venus. It is known (Harteck and Dondes, 1963) that when carbon suboxide is formed at high temperatures (250-300°C), it appears blackened due to the presence of carbon. Thus, on the surface of Venus, over geologic ages, carbon also may have been formed by decomposition of suboxides.

Since carbon suboxides are extremely hydroscopic, small amounts of water which might be present would soon be entirely consumed. It should be noted that, in the absence of water vapor, gaseous volcanic exhalations, such as SO_2 which on Earth would be washed out of the atmosphere by rain, would accumulate in the Venus atmosphere and contribute to the clouds; a fact which may explain their observed yellowish color. The possibility of the presence of gaseous sulfur has been suggested (Suess, 1963) and this may exist in thermodynamic equilibrium in the Venus atmosphere, provided that the surface temperature is reasonably high. However, if any part of the surface is cold, sulfur would condense out.

From a chemical point of view, it is interesting that the Venus atmosphere is a ''neutral'' atmosphere, being neither oxidizing nor reducing. This situation could be understood if the atmosphere had been initially reducing with excess CO, as mentioned above. This CO would have been transformed by ionizing radiation into carbon suboxide polymer, which would condense out, and CO_2, which would remain in the atmosphere. Other possible components of the clouds may include polymers of CN and CNO which are known to be formed by the action of ionizing radiation on CN and mixtures of CN and O_2 as mentioned above. In the latter case a pale yellow polymer $(CNO)_x$ is formed. The chemical nature of these compounds is such that over geologic ages they would

tend to decompose rather than to accumulate, reaching an equilibrium steady state. It should be noted that, as previously discussed, it is extremely unlikely that the clouds can be ice crystals as Sagan (1961) has suggested.

It is also of interest to observe that Venus, like the Earth, is in a stationary state photochemically because radiation equilibrium is attained. Jupiter and other more distant planets are not in such a stationary state, however, and there will be irreversible decomposition of hydrocarbons, ammonia, etc.

CONCLUDING REMARKS

The atmosphere of Venus is at present a rather controversial subject. To clarify some of the aspects, a series of conditions which may exist on Venus have been simulated. Experimental measurements have been made of the absorption coefficients of CO_2, CO, O_2, and other gases in the region from 1850 A to longer wavelengths. The behavior of CO_2 under the impact of ionizing radiation from pressures of one atmosphere down to a few hundred microns has been studied and extrapolation made to the region of chemosphere. Reaction mechanisms which may occur and be of major importance in the Venus atmosphere have been discussed. As an alternate to the currently popular thermal origin of the observed microwave radiation emitted from Venus, a chemical source is suggested. Light-emitting chemical reactions of the type believed to occur on Venus are under study. Preliminary results show that microwave radiation in the 3 cm wavelength region is emitted from the CO_2 discharge. Additional experiments in these areas are in progress.

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